

Gas Chromatography of Phenylphenols and Chlorophenylphenols on a Silicone Nitrile Column

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A variety of liquid phases has been used in the gas chromatographic analysis of phenolic compounds. Substrates of widely varying polarity, from paraffinic to highly polar materials, have been found effective by virtue of differences in retention between ortho-substituted phenols and phenols unsubstituted in the ortho positions, but having the same boiling point. This phenomenon has been termed the "ortho effect" (2). On a polar column ortho-substituted phenols are eluted more rapidly because of reduced interaction between the phenolic hydrogen and the stationary phase. On a non-polar column phenols with alkyl substituents in the ortho position are retained longer than those of equal boiling point but without ortho substitution. Summaries of the substrates used for phenol separations may be found in papers by Fitzgerald (1) and Kolof et al (4).

Gas chromatographic separation of phenols is of interest to this laboratory because a number of phenolic

compounds are components of disinfectant formulations for which analytical procedures are required. The thermal stability and highly polar nature of silicone nitrile polymer suggested a trial of this material for the separation of the less volatile phenols. A silicone nitrile column prepared from GE XE-60 was found to give excellent separation of orthophenylphenol, 4-chloro-2-phenylphenol and 6-chloro-2-phenylphenol. It has been in use now for many months in the analysis of a disinfectant prepared from the sodium salts of these three phenols. A list of retentions is here presented for phenylphenols, chlorophenylphenols and other phenols which have been chromatographed on the XE-60 column.

Experimental

A 6 ft. x 1/4 in. copper column was packed with 10% XE-60 deposited

on Diatoport S, 60-80 mesh. A non-polar column of the same length packed with 10% SE-30 on Chromosorb W was used for comparison. The instrument used was the F&M Model 720 chromatograph with the following operating conditions: Helium, 30 lbs. pressure, 80 mls/min.; Temperatures, injection port 300°C; Column 210°C, Detector 250°C; Bridge power, 155 ma; Attenuation, x4; Chart speed, 0.5 in/min; Sample size, 10 µl of a solution containing 50 µg/µl for the retention data.

Discussion

The separation of o-phenylphenol, 4-Cl-2-phenylphenol and 6-Cl-2-phenylphenol is shown in Figure 1 with p-chlorophenol as an internal standard. Peak heights relative to the standard were used for the quantitative analysis. A comparable separation has been obtained on 15% butanediol succinate (3),

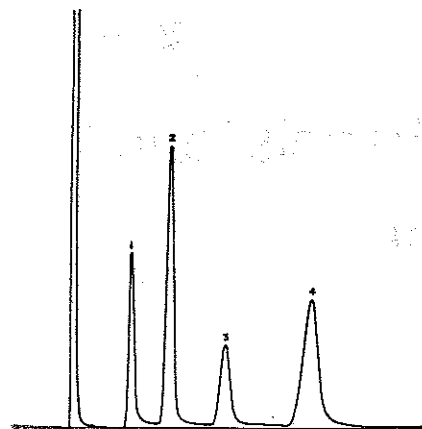


Figure 1. Chromatogram showing separation of 1) p-Chlorophenol, 2) o-Phenylphenol, 3) 6-Cl-2-phenylphenol, and 4) 4-Cl-2-phenylphenol on the GE XE-60 column.

which would be less satisfactory for high boiling compounds because of its lower temperature limit. Good resolution of the mixture was obtained in this laboratory with 10% carbowax 20M and with 10% diethyleneglycol succinate, but retention times were excessively long on both columns.

Table I lists the retention times of the phenols on both XE-60 and SE-30. The three chlorophenylphenols provide a striking example of the effect of double ortho substitution; the retention time of 6-Cl-2-phenylphenol is greatly reduced, although its boiling point is intermediate between the other two. A similar slight reduction on the SE-30 points to some polarity in that substrate. Notable also is the retention reversal of p-phenylphenol and 2-Cl-4-phenylphenol; the latter is eluted well ahead of the former despite a boiling point 15°C higher. The 2-Cl-4-phenylphenol can be separated from the other chlorophenylphenols on Apiezon L.

It was of interest to study the separation of other isomers on XE-60, especially meta and para isomers which are particularly difficult to separate. In a study of isomeric phenols, Lindsay Smith et al (5) found tris (2-4-xylenyl) phosphate and diethyleneglycol adipate to be effective, but retention times were frequently an hour or longer under

Table I. Retention Times of Phenols on XE-60 and SE-30 Columns

Compound	Boiling Point °C	Retention Minutes	XE-60 Relative	Retention Minutes	SE-30 Relative
Phenol	182	1.25	1.00	0.73	1.00
o-Phenylphenol	275	4.80	3.84	3.28	4.49
p-Phenylphenol	308	18.5	14.8	5.51	7.55
4-Cl-2-phenylphenol	312	11.20	8.96	6.08	8.33
6-Cl-2-phenylphenol	318	7.43	5.94	5.81	7.96
2-Cl-4-phenylphenol	323	11.16	8.93	6.39	8.75
m-Chlorophenol	214	3.04	2.43	1.14	1.56
p-Chlorophenol	217	3.09	2.47	1.15	1.58
α -Naphthol	280	9.34	7.47	3.19	4.37
β -Naphthol	286	10.81	8.65	3.29	4.51
o-Nitrophenol	217	1.48	1.18	1.13	1.55
m-Nitrophenol	—	10.19	8.15 ^a	2.61	3.58
p-Nitrophenol	279	11 (approx)	— ^{a,b}	3.17	4.34
o-Hydroxyphenol	240	1 to 3	— ^b	1.25	1.71
m-Hydroxyphenol	280	9.98	7.98	1.40	1.92
p-Hydroxyphenol	286	8.56	6.85	1.40	1.92

(a) Column at 230°C

(b) No sharp peak obtained

the conditions used. With the XE-60 column, mixtures of the naphthols and of m- and p-hydroxyphenol were resolved sufficiently for analysis, but not completely separated, in about 10 minutes, m- and p-chlorophenol were not resolved, and m- and p-nitrophenol were not eluted at 210°C. The column temperature was then increased to 230°C and the injection port decreased to 270°C to avoid decomposition. At these temperatures the m-nitrophenol gave a satisfactory chromatogram but the p-nitrophenol was eluted in the shape of a broad hump. o-Hydroxyphenol likewise showed evidence of reaction with a short and shifting retention time. It is not known whether additional column priming would have overcome this effect and improved the peak shape.

From the results obtained with these compounds it appears that

silicone nitrile is good polar material for phenolics, with some degree of selectivity for isomers, and is worthy of a trial when such a separation is required.

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